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DISPENSER FOR CONTROLLED RELEASE OF PHEROMONES
[Dispenser zur kontrollierten Freisetzung von Pheromonen]

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The present invention relates to a dispenser for the controlled /2* release of pheromones.

Pheromones are messenger materials, which trigger a certain reaction within a species. Due to the species-specific effect, attempts were made at an early stage to use such materials for plant protection. The sexual pheromones are of particular interest in this regard. Pheromones were first used commercially in baited traps for monitoring and mass trapping. Another technique involving the use of pheromones in plant protection, the so-called "mating disruption" method, has been developed in recent years. It has been shown in numerous tests that pests can be controlled using this technique.

A prerequisite for the successful use of sexual pheromones in mating disruption is a well functioning dispenser, i.e., a system that releases the active ingredient over a long period of time at a constant release rate. Many such systems are described in the literature and they may be divided into two categories:

1. Matrix systems
2. Reservoir systems

In matrix systems, the active ingredient is homogeneously distributed in a matrix. Due to this structure, the release rate is not linear, but decreases over time. Reservoir systems do not have this disadvantage, since the pheromone is in a reservoir and is

* Numbers in the margin indicate pagination in the foreign text.

released by diffusion through a wall of constant thickness. Thus, unlike matrix systems, reservoir systems have a constant release rate and are superior in release characteristics and often in duration of release, as well.

Three reservoir systems are found in the prior art:

1. Hollow fiber systems, microcapsules
2. Polyethylene containers
3. Film bags (with or without fillers)

Hollow fibers (US 4,017,030) and microcapsules (EP 0 141 584, US 2,800,457, US 3,577,515, JP 6 140 213) are systems with very small reservoirs and, thus, they frequently have only a limited period of action. Moreover, manufacturing costs are usually quite high.

Polyethylene dispensers in tube (EP 0 243 007, EP 0 160 151, EP 0 194 934, US 4,600 146, US 4,734 281) and ampoule form (DE 3 640 880) have been used successfully in "mating disruption" methods for some time and, compared to other dispensers, they generally have a stable and efficient suspension apparatus.

The disadvantage of tube dispensers (EP 0 160 151, etc.) is the dependence of their release rate on the respective fill level. Consequently, there is a decrease in the amount released over time and, thus, nonlinear release behavior.

Due to their high plastic content, the pheromone ampoules described in DE Patent 3 640 880 have a high release rate in the initial period after distribution. During storage, the plastic

absorbs large quantities of active ingredient, which is then released after distribution. An additional disadvantage of these double or multi-chambered ampoules is that, due to production reasons, all the chambers must be made of the same material. For simultaneously combating two or more pests, the corresponding pheromones must be released at approximately the same time and at approximately the same release rate. If the material is optimized to the desired release rate of one pheromone, then the second pheromone may be delivered far too rapidly or too slowly. The release rate must then be corrected by adding solvent, taking into account deviations from the linear release behavior.

Compared with film dispensers, for example, polyethylene dispensers generally also have the disadvantage of complex production processes and high manufacturing costs. For these reasons and because of the lower amount of plastic, the present invention uses films for producing the dispenser.

Film bags for releasing fragrance materials and active ingredients have already been described in the literature. However, these systems typically have a very large evaporation surface, of more than 30 cm². When polyethylene and polypropylene films are used, which are often indispensable for welding the bags, the diffusion rate must be reduced, in order to prevent an increased rate of release. As seen below, this can be accomplished in various ways.

The use of film bags to release perfumes was described in 1974 in US Patent 3,951,622. In subsequent patent EP 0 194 896, the application is extended to pheromones, albeit in the form of solutions in alcohols. Such solvent additives dilute the active ingredient and, thus, reduce the diffusion rate. This method of release control is problematic, however, when solvent and active ingredient possess different diffusion rates. Over time, the composition of the solution changes and the release rate is not constant.

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Film bags are also described in patents DE 2 832 248, DE 2 945 655, and EP 0 019 010. Here, the active ingredient is in a porous or pasty matrix, enclosed in the film bag, for delaying release. This has the disadvantage that the pheromone is not completely released and the negative release behavior of the matrix system again determines the release characteristics of the dispenser.

In Patent EP 0 342 126, the delay in the diffusion rate is achieved by using laminated films. In addition to polyethylene, the film contains polyvinylidene chloride as a diffusion-retarding layer. Such laminated films often create problems in practical applications, since, for a reproducible release rate, considerable demands must be placed on the quality of the film. Fluctuations in the thickness and/or density of the laminate, in particular in the frequently very thin film layer that determines the diffusion rate, result in sharp differences in release behavior. Since, in general, the films are not

optimized for the diffusivity, but for their barrier properties, fluctuations may well result in the production of laminated films that have no effect on the barrier properties, but significantly change the diffusion properties of the film.

A film bag for releasing perfumes and fragrances and production of same are described in Patent DE 3 149 508. Unspecified aroma-tight and aroma-permeable films are welded to form a bag, whereby the permeable film is prevented by a removable aroma-tight film from giving off fragrance material until the dispenser is used.

Also for preventing release during storage, Patent DE 3 490 012 uses a special film comprising a barrier layer and a permeable layer, which are connected by a paper layer. When the barrier film is removed, the paper layer is torn apart, so that easy removal of the film is possible. The unspecified container is provided for releasing the fragrance material. Problems arise related to the paper layer whose residue, which remains on the permeable film, can have unforeseeable effects on the diffusion of the contents and, thus, on the release rate. Moreover, the use of intermediate paper layers for the above-mentioned application was previously described in Patent US 3,083,821. More recently, it has become possible to develop specific sealing coats, which result in peelable laminates.

For practical use of a pheromone dispenser, simple and easy distribution must be provided. However, the dispenser should also be fastened in such a way that it is not torn loose from the branches or

wires, even when harvesting machines are used. None of the film dispensers presented in the prior art can meet this requirement, for three reasons:

1. Due to the lability of the films, a stable suspension apparatus with sufficient strength cannot be mounted. It is not enough, as with the bottles in DE 3 149 508, which by the way are for use indoors, to punch a hole for suspension. To attach the device to a branch or wire, a string or a wire would have to be passed through the hole and tied to the branch. This requires an additional and time-consuming work step.
2. When automatic harvesting machines are used, the dispensers are at times subjected to large forces, so that they may tear if then films are used.
3. Film bags, which usually have a large evaporation surface, tend to inflate in strong sunlight when used in open spaces. Occasionally, the bags have been found to tear.

Finally, US-Patent 4,562,794 describes a dispenser for controlling animal pests. A membrane permeable to the pesticide is placed on a stable plastic plate. Between the membrane and the plate is the active ingredient, embedded in a porous matrix. This results in the aforementioned disadvantages in release behavior. The dispenser may be fastened, for example, to the ears of cattle.

In summary, the film systems described in the prior art for use in open spaces have insufficient or no suspension devices. Adjustment of the desired release rate is achieved by methods that are not reproducible or do not permit constant release rates.

The object of the present invention was therefore to develop a pheromone dispenser based on plastic films, said dispenser having a linear release characteristic. With the exception of stabilizers and UV absorbers, the pheromone components should be present in the container without additives, i.e., solvents, porous solids, etc., and should be released through a permeable membrane. The dispenser should be equipped with a stable, but easily manageable suspension device and it should withstand storage times without loss. It should be possible to use the dispenser against various pests at the same time, with an optimal release rate for each of the pheromones used.

This object was achieved by the characteristics of Claims 1 /4 through 11.

As described above, care must be taken when using laminated films in bag dispensers, since high requirements are placed on the uniformity of such laminated films. Thus, due to quality assurance in production, single layered, at most two-layered, standard films are best suited for such applications with high requirements on the consistency of the diffusion rate for a certain compound. However, such films based on polyethylene or polypropylene have a high pheromone permeability. In the case of bags with large evaporation

surfaces, this results in excessively high release rates. To avoid using additives to the active ingredient, which reduce the diffusion rate (see above), we have attempted to regulate the release rate by way of the available evaporation surface. Surprisingly, it has been found that this is possible, without sticking or dripping on the part of the dispenser. Both might be expected, due to the high diffusion rate, but they are not observed with the with the pheromones used.

It has proven particularly favorable to shape the container chambers in such a way that a large-volume and a small-volume reservoir are available, with a small and a large evaporation surface, respectively. The small reservoir is fed by the large reservoir and, due to the large evaporation surface, it is primarily responsible for the release rate. In our experiments, the container structure mentioned above resulted in constant release rates. Only when the large reservoir is completely empty does the supply rate begin to slow.

The surface reduction is accomplished by using a stable, pheromone-impermeable film, which is shaped into a reservoir by punching, deep drawing, etc. This container is filled with the active ingredient and closed off by a single-layer or two-layer permeable membrane. In this way, only the surface of the film covering the pheromone-containing container is available for evaporation. It was also found that, by varying the shape of the container while maintaining the same volume, various surfaces and, thus, various

release rates can be achieved. Of course, the release rate can also be varied by upper films, differing in material or thickness.

By reducing the evaporation surface, the dispenser can be made very compact and thus, compared to the film bags previously described, it offers a small engagement surface when harvesting machines are used. Apart from the container opening, which is covered by the permeable top film, the dispenser comprises the stable bottom film and, thus, it is more resistant to external forces.

As we have shown previously, the ratio of permeable surface to volume is of crucial importance for a linear release rate. In the present dispenser, this ratio is very low and, thus, it is optimized for a linear release rate. The large volume of the container is offset by a small evaporation surface.

The use of a stable, pheromone-impermeable bottom film has two additional advantages. First of all, the high release rate observed when ampoule dispensers are first hung is surprisingly not found with the dispensers of this invention. This is due to the fact that the greater part of the dispenser is made of a plastic that is not accessible to the active ingredient. In this case, concentration of the pheromone in the plastic during storage, as with polyethylene tubes or polyethylene ampoules, is not possible or possible only to a very limited extent.

Secondly, with its rigidity, the film has the advantage that suspension devices can be fashioned from it that are easily mounted

while, at the same time, they hold so firmly that they do not fall off, possibly contaminating the crops, even when automatic harvesting machines are used.

We have found that polyamide, polyester, and polyvinyl chloride films and laminated films thereof are suitable for use as bottom films for the pheromone dispensers we have developed. Films comprising a plurality of layers are not problematic in this context, since only the barrier properties of the film, which can be provided with a certain layer thickness, are of importance here. Laminated films with barrier layers of polyvinyl alcohol, ethylvinyl alcohol, or polyvinylidene chloride can also be used. Biodegradable materials, such as starch, polyhydroxy butyric acid, etc., and laminated films thereof may also be used. The thickness of the film is preferably greater than 200 μm , in order to provide sufficient stability for the suspension device.

To protect the pheromones, some of which are unstable to UV light, both the lower and the upper film can be colored with pigments.

The selected dispenser structure provides an additional advantage, as well. Only the permeable upper film is responsible for releasing the active ingredient. If one wishes to prevent release, for example during storage, it is a relatively simple matter to suppress pheromone release by placing or laying a pheromone-tight film on top. Before use, the protective film is removed once again

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and the dispenser begins to operate. If the protective film is only partially removed from the release surface, it provides an elegant way to affect the amount of release surface that is available. The same films as described for the lower film can be used as materials, but with a smaller thickness.

The design of the dispenser with two or more chambers produces the advantage that two or more pests can be treated at the same time, in a single work operation. This is important, since there are more and more cultivated areas in which a plurality of pests are present. As previously mentioned, in this context, too, the selected design of the dispenser has advantages. While with the double or multiple chamber ampoules described in Patent DE 3 640 880 all chambers are made of the same material, due to production considerations, with the present invention and the proper choice of dispenser shape, each chamber can be covered with a different top film, so that the release rates of the individual pheromones are coordinated with one another. It is also possible to undertake such regulation by way of the release surface by providing the dispenser with chambers of different sizes.

As we have found and documented in the following examples, the inventive dispensers have a constant release rate of an order of magnitude sufficient to last several months.

Embodiments will be explained in greater detail below, with reference to drawings 1 and 2.

Figures 1a and 1b show front and side views of an inventive pheromone dispenser **1** with, for example, two chambers **2**. Round punched hole **3** in the upper portion of the dispenser accommodates the fastening device (branch, wire, etc.), which is led through slot **4**. The stability of lower film **5** guarantees a firm hold of the dispenser on the fastening points. Indentations **8** also provide lateral stabilization of the suspension hoop. Container **2**, made of pheromone impermeable under film **5**, accommodates the pheromone and is closed off by permeable film **6**. Using appropriate mechanical equipment, the dispenser can be made in such a way that each chamber has a different top film **6a** and **6b**. In this way, the different diffusion and release rates of the two pheromones can be evened out.

Figures 1c and 1d show a side view of inventive dispenser **1** with, for example, 2 chambers. In this case, the shape of container **2** is selected in such a way that a large-volume reservoir **2a** with a small evaporation surface is placed beside a small-volume reservoir **2b** with a large evaporation surface. The shape of the transition from the large to the small reservoir can be step-like (1d) or continuous (1b).

Figure 2a shows a front view of another inventive dispenser **1**, which is also equipped with two chambers **2**. The chambers differ in their release surface, whereby two pheromones that diffuse at different rates can be matched to each other using the same top film

6. Again, the suspension device receives its stability from the thick lower film and is additionally stabilized by indentations 8.

Figure 2b shows a side view of the dispenser. Chambers 2 are made with different depths in order to accommodate the same volume of pheromone.

Figure 3 shows an enlarged view of the film structure of an inventive dispenser when the latter is covered by a protective film 9 for storage. Protective film 9 is either simply placed on top or it is peelably welded (bonded) and can be removed before use.

The different release characteristics of laminated matrix system (I), polyethylene tube dispenser (II), and inventive film dispenser (III) are shown in Fig. 4. Because of its structure, matrix systems have a first order release rate, i.e., the amount of active ingredient released decreases over time. As a reservoir system, the tube dispenser is superior to the matrix system in this respect. However, due to the large evaporation surface, which decreases over time along with the fill level, the release rate gradually drops.

In contrast, the film dispenser has a very constant release rate, which also remains unchanged over a long period of time. Only when the reservoir is practically empty does the release rate drop.

Figure 5 shows a comparison of the evaporation curves of a dispenser in accordance with this invention (A) and a polyethylene container in ampoule form (B). With the ampoule dispensers, which have a high plastic content, the ability of the plastic to store the

pheromone results in the high release values at the beginning of pheromone release. On the other hand, the low permeable plastic content of the film dispenser is the reason why no high values are determined with the inventive dispenser when it is first hung out. During the further course of active-ingredient release, a linear release behavior is found with both reservoir dispensers.

Figure 6 shows the influence of different evaporation surfaces on the release behavior. Both dispensers were charged with 300 mg Z9:12Ac pheromone, but were provided with different evaporation surfaces. Dispenser I has a permeable surface of 1.8 cm², dispenser II 3.1 cm². The larger evaporation surface causes an increased release rate in dispenser II.

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The constant release rate of the inventive dispenser is documented once again, based on the following examples.

Example 1

The dispenser is made of a PVC/PE lower film (250 µm) and a permeable upper film of polyethylene (70 µm) and it is charged with 300 mg Z9:12Ac-pheromone. The dispenser is suspended under laboratory conditions and the loss of active ingredient determined gravimetrically each week.

Zeit (Wochen)	Restgehalt (%)	durchschnittliche Abgaberate (mg/(d* Disp.))
0	100	
1	94	2.6
2	89	2.3
3	83	2.3
4	78	2.5
5	72	2.4
6	67	2.3
7	61	2.8
8	55	2.4
9	50	2.3
10	44	2.4
11	38	2.5
12	33	2.4
13	27	2.4
14	21	2.5
15	16	2.2

Key:

Time (weeks)	Residual content (%)	Average release rate (mg/(d* dispenser))

Example 2:

The dispenser is made of a polystyrene/EVOH/PE laminated film (250 µm) and a permeable upper film of polyethylene (50 µm) and it is charged with 500 mg Z9/Z11:14Ac pheromone. The dispenser is suspended under laboratory conditions and the loss of active ingredient determined gravimetrically each three weeks.

Zeit (Wochen)	Restgehalt (%)	durchschnittliche Abgaberate (mg/(d* Disp.))
0	100	
3	82	2.0
6	83	2.0
9	75	1.9
12	68	2.1
15	58	2.0
18	51	1.8

Key:

Time (weeks)	Residual content (%)	Average release rate (mg/(d* dispenser))

Claims

1. A dispenser for the controlled release of pheromones, in particular sexual pheromones, characterized in that a dimensionally stable container, which is made of a material that is impermeable to the pheromone and serves as a pheromone reservoir having a volume of 0.5 to 2.5 ml, is closed off by means of a pheromone-penetrable film, which is responsible for the pheromone release and has a release surface of no greater than 10 cm².

2. A dispenser as recited in Claim 1, characterized in that a /7 chamber of the dimensionally stable container is divided into a large-volume reservoir, which accounts for only a small portion of the evaporation surface, and a small-volume reservoir, which accounts for the greater portion of the evaporation surface and is fed with pheromone from the large reservoir.

3. A dispenser as recited in Claim 1 and Claim 2, characterized in that the dimensionally stable container is made of a film having a thickness greater than 150 μ m and is provided with a stable suspension device.

4. A dispenser as recited in Claims 1 through 3, characterized in that the pheromone is located in the reservoir without additives, such as solvents or fillers.

5. A dispenser as recited in Claims 1 through 4, characterized in that the pheromone-impermeable film or laminated film consists of at least one layer of polyester, polyamide, polyvinyl chloride,

polyvinylidene chloride, polyvinyl alcohol, polyethylvinyl alcohol, or biodegradable polymers, such as starch or polyhydroxybutyric acid.

6. A dispenser as recited in Claims 1 through 5, characterized in that the pheromone-permeable cover film has a thickness of 20 - 150 μm and consists of at least one layer of polyethylene, polypropylene, copolymers of polyethylene and polypropylene with vinyl acetate, starch, or polyhydroxybutyric acid.

7. A dispenser as recited in Claims 1 through 6, characterized in that the dispenser consists of two or more chambers for simultaneously applying two or more pheromones in one operation.

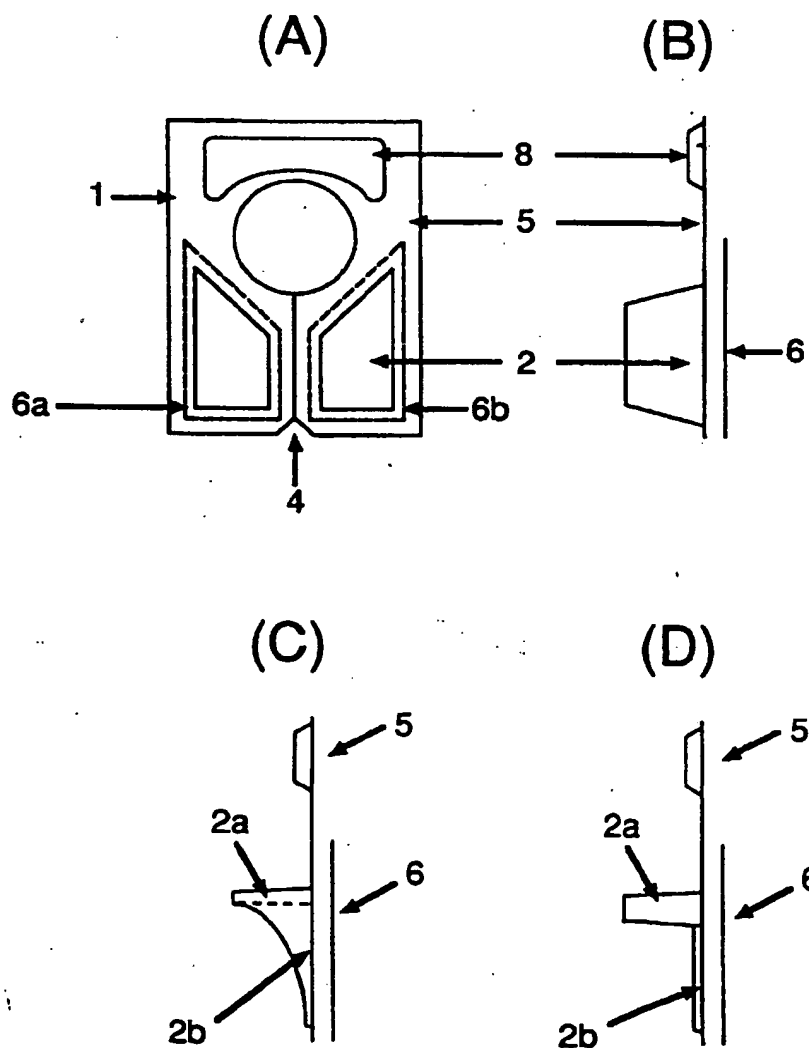
8. A dispenser as recited in Claims 1 through 7, characterized in that, for adjusting the release rate, the chambers of a dispenser can be equipped with different cover films and different release surfaces.

9. A dispenser as recited in Claims 1 through 8, characterized in that a film placed over the permeable membrane, which is impermeable to the pheromone, prevents evaporation of the pheromone during storage.

10. A dispenser as recited in Claims 1 through 9, characterized in that the protective film is made of the materials listed under Claim 3, as well as aluminum or aluminum laminates with polyethylene and polypropylene and it can be removed completely or partly from over the small-volume reservoir before the dispenser is used.

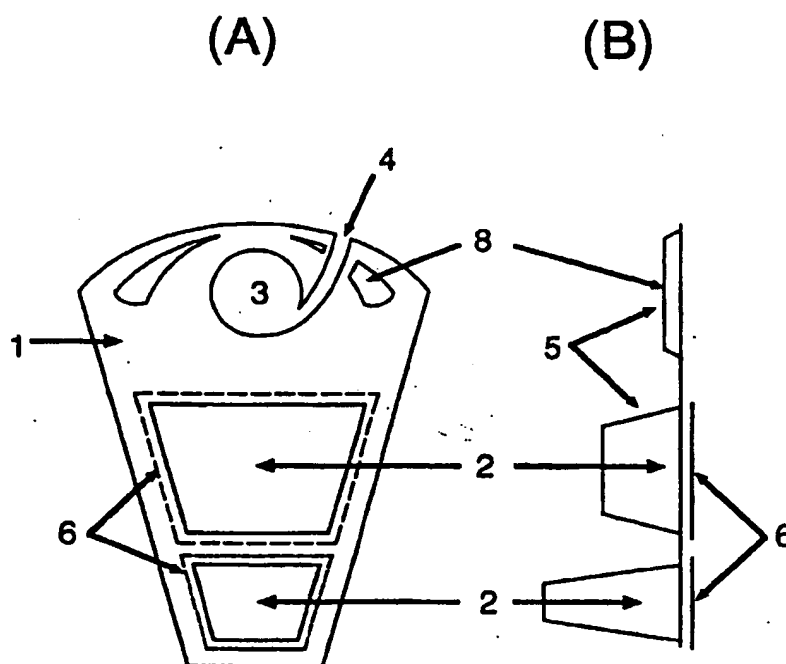
11. A dispenser as recited in Claims 1 through 10, characterized in that the protective film is applied or peelably sealed or adhesively bonded on.

FIG.1



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FIG.2



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FIG.3

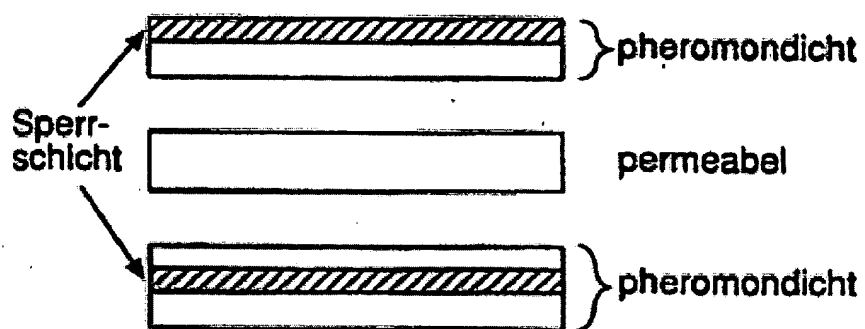


FIG.4

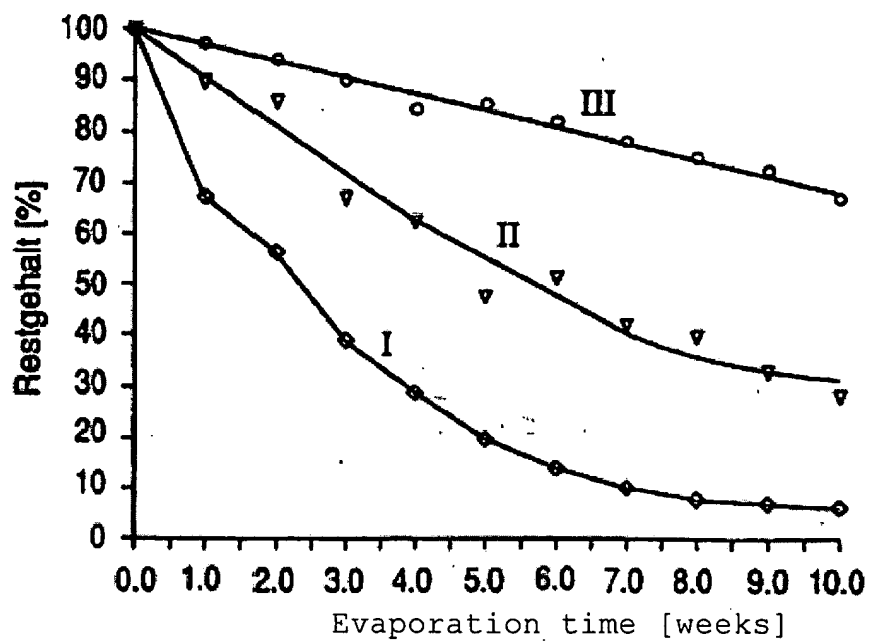


FIG.5

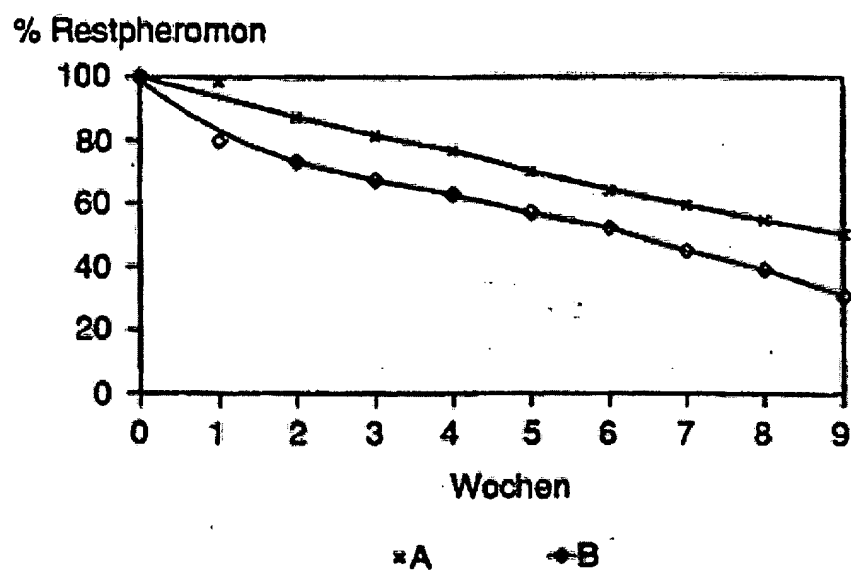
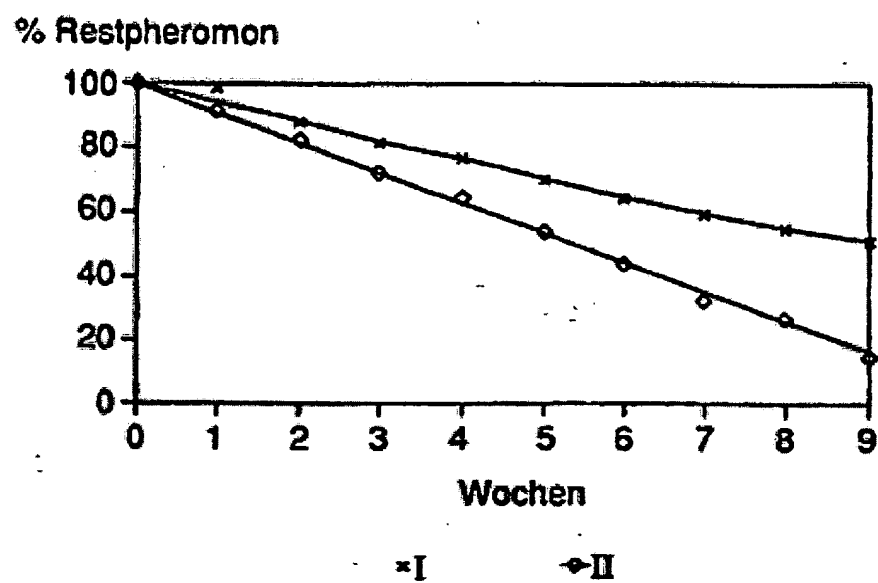


FIG.6



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